COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Stereoselective formation of dinuclear complexes with anomalous CD spectra†

Shane G. Telfer,*[a] Reiko Kuroda*[ab] and Tomohiro Sato[a]

[a] *JST ERATO Kuroda Chiromorphology Project, Park Bldg., 4-7-6 Komaba, Meguro-ku, Tokyo 153-0041, Japan. E-mail: shane.telfer@chiromor2.erato.rcast.u-tokyo.ac.jp; Fax: +81 3 5465 0104; Tel: +81 3 5465 0104*

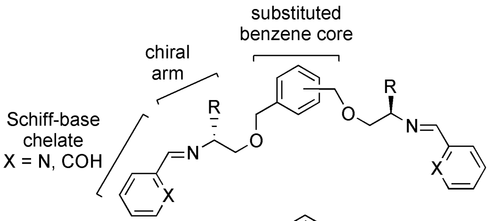
[b] *Graduate School of Arts and Sciences, University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan. E-mail: ckuroda@mail.ecc.u-tokyo.ac.jp; Fax: +81 3 5454 6600; Tel: +81 3 5454 6600*

Received (in Cambridge, UK) 3rd February 2003, Accepted 13th March 2003
First published as an Advance Article on the web 27th March 2003

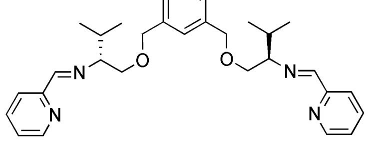
A novel chiral tetradentate Schiff base ligand forms dinuclear Λ,Λ-$[M_2L_2Cl_2]^{2+}$ complexes with high diastereoselectivity; the complexes exhibit anomalous CD spectra due to exciton coupling of chromophores located on different metal centres.

The stereoselective synthesis of coordination compounds is a burgeoning field of chemistry.[1] This can be in part ascribed to the importance of transition metal complexes in asymmetric catalysis, and to recent developments in metallosupramolecular chemistry. The latter has been a particularly strong stimulus as the combination of multiple stereogenic metal centres in polynuclear complexes gives rise to a large number of possible diastereomers. Within the field of metallosupramolecular chemistry, some principles are beginning to emerge with respect to the rational synthesis of polynuclear complexes.[2] In this context, the relative orientation of chelating groups and the nature of the bridge between them are among the most important factors.

In order to further explore the issues of stereoselectivity and rational design highlighted above, we are interested in the family of chiral ligands depicted below (**1**). The ligands are centred around a benzene core with chiral arms radiating out to Schiff base chelate groups. These arms can be arranged in an *ortho*, *meta*, *para*, or 1,3,5-fashion around the benzene core. The influence of their relative orientation on the structure of the resulting metallosupramolecular assembly can thereby be systematically investigated. The chiral arms are derived from amino alcohols, thus a large number of enantiopure candidates are readily available. In this communication we wish to report on the coordination chemistry of ligand **2**.



1



2

Ligand **2** was prepared via the nucleophilic displacement of bromide from *meta*-bis(bromomethyl)benzene by the anion of L-valinol, followed by condensation of the resulting amine with pyridine-2-carboxaldehyde. It was then reacted with a range of cobalt(II) and nickel(II) salts. During these investigations a peculiar dependence of the UV-vis and CD spectra on the nature of the counter anion was noted. Fig. 1 shows the CD spectra of 1:1 mixtures of **2** with a variety of metal salts.† It can be seen that perchlorate salts lead to a positive CD signal around 295 nm, while chloride salts produce a negative CD signal at this wavelength. Addition of one equivalent of Bu_4NCl to the solutions containing $M(ClO_4)_2$ inverted the positive CD signal; the resulting spectrum being superposable on that of the solutions containing the corresponding MCl_2 salt. However, the reverse experiment–addition of Bu_4NClO_4 to the solutions containing MCl_2–had no effect on the CD spectrum. Moreover, the addition of fluoride or bromide ions to the solutions containing $M(ClO_4)_2$ did not invert the CD signal, nor did the addition of other anions such as acetate, thiocyanate, or hydroxide.

The dramatic influence of the presence of chloride ions on complex formation was also evidenced by electrospray mass spectroscopy. The ES-MS spectrum of a solution of $M(ClO_4)_2$ and **2** (1:1 ratio) displayed just two peaks which corresponded to $[M(\mathbf{2})]^{2+}$ (100%) and $[M(\mathbf{2})ClO_4]^+$ (5–30%). On the other hand, spectra of solutions containing MCl_2 displayed just one peak, which could be attributed to the $[M_2(\mathbf{2})_2Cl_2]^{2+}$ complex ion.

The formation of such a dinuclear complex was confirmed by X-ray crystallography,‡ revealing a $[Co_2(\mu\text{-}Cl)_2]$ diamond-shaped core (Fig. 2). The Co–Co separation is 3.54 Å and the average Co–Cl distance is 2.44 Å.[3] Two molecules of **2** also bridge the two cobalt(II) centres in a side-by-side arrangement with Co–N distances in the range 2.12–2.13 Å. The overall geometry around the cobalt(II) centres is approximately octahedral, and both metal centres adopt the Λ configuration. The tilting of the benzene rings lowers the overall symmetry of the complex cation from D_2 to approximate C_2, with psuedo-twofold symmetry around both the Co–Co and Cl–Cl axes. Large, chiral, hydrophobic cavities are present with the structure, as highlighted by the space-filling model presented in

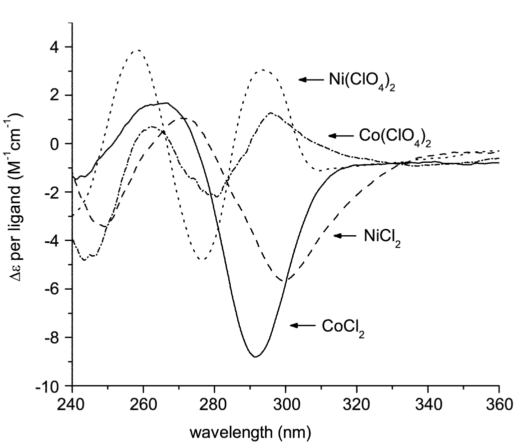


Fig. 1 CD spectra of a 1:1 mixture of ligand **2** and a range of metal salts recorded in CH_3CN.

DOI: 10.1039/b301267k

---

† Electronic supplementary information (ESI) available: UV-vis and ^1H NMR spectra. See http://www.rsc.org/suppdata/cc/b3/b301267k/

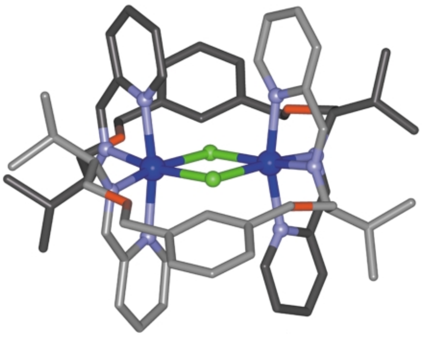


Fig. 2 X-ray crystal structure of the non-hydrogen atoms of the Λ,Λ-$[Co_2(\mathbf{2})_2Cl_2]^{2+}$ cation. The carbon backbones of the two ligands are presented in different shades of gray. Blue = Co, green = Cl, blue-gray = N, red = O.

Fig. 3. The charge of the complex cation is balanced by a $[CoCl_4]^{2-}$ counter anion which has the expected tetrahedral geomtery, and exhibits Co–Cl distances in the range 2.26–2.30 Å. The presence of this anion accounts for the deep-green colour of the crystals.

An ^{1}H NMR spectrum was recorded of crystals of Λ,Λ-$[Co_2(\mathbf{2})_2Cl_2]CoCl_4$ dissolved in CD_3NO_2.† A set of 13 signals was observed, paramagnetically shifted over a range of 155 ppm. This spectrum is consistent with retention of the structure deduced by X-ray crystallography, and implies that formation of Λ,Λ-$[Co_2(\mathbf{2})_2Cl_2]^{2+}$ in solution is highly diastereoselective (d.e. > 95%). A plausible explanation for the high diastereoselectivity lies with the orientation of the bulky isopropyl units of the ligand. From the X-ray crystal structure it is apparent that inversion of the chiral centres of **2** would force the isopropyl groups towards a pyridine ring of the other ligand, resulting in an energetically unfavourable steric clash.

The CD spectrum of crystals of Λ,Λ-$[Co_2(\mathbf{2})_2Cl_2]CoCl_4$ were recorded in both the solid state (KBr disc) and in solution (dissolved in CH_3CN). The spectra were very similar to that displayed in Fig.1 for a 1 : 1 mixture of $CoCl_2$ and ligand **2**. The bisignate curve in the 260–320 nm range is strongly suggestive of an exciton coupling effect.[4] It is well known that the placement of multiple di-imine units around an octahedral metal centre enables exciton coupling of the degenerate π–π*transitions of these chromophores.[5] The sign of the resulting exciton couplet can be directly correlated with the absolute configuration of the metal centre. Based on this correlation, coupling of the π–π*transitions of the di-imine units of **2** chelated to a Λ metal centre would be expected to bring about a bisignate curve which is *positive* at higher wavelengths.§ While this is observed for solutions containing $M(ClO_4)_2$ salts, the opposite is actually seen for Λ,Λ-$[M_2(\mathbf{2})_2Cl_2]^{2+}$.

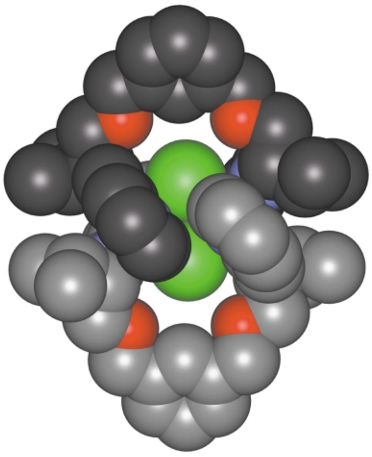


Fig. 3 Space-filling representation of the Λ,Λ-$[Co_2(\mathbf{2})_2Cl_2]^{2+}$ cation (top view).

How may we resolve this apparent anomaly? The CD spectra of the solutions containing **2** and $M(ClO_4)_2$ can be simply accounted for by the formation of mononuclear complexes which have a preference for the Λ configuration at the metal centre. On the other hand, inspection of Figs. 2 and 3 reveals that the pyridylimine chromophores located on *different* metal centres of Λ,Λ-$[Co_2(\mathbf{2})_2Cl_2]^{2+}$ are actually held in relatively close proximity.¶ Thus, a further two 'internuclear' exciton coupling modes are 'switched on' by formation of the dinuclear complex. Analysis of the relative orientation of the electric dipole transition moments for these internuclear couplings predicts that they will both give exciton couplets which are negative at higher wavelengths. If the combined intensity of these internuclear couplings is greater than that of the intranuclear coupling, this rationale accounts for both the sign of the observed CD signal and its relatively low intensity. Preliminary results of theoretical calculations on this system lend support to this argument. These results are highly pertinent to other chiral systems which have multiple interacting chromophores,[6] however, it appears that this effect has not previously been considered.

We thank Dr Nobuo Tajima for performing the electric dipole transition moment calculations, and the JSPS for a fellowship to SGT.

Notes and references

‡ *Crystal data* for $[Co_2(C_{30}H_{38}N_4O_2)_2Cl_2](CoCl_4)\cdot(CH_3CN)_3\cdot H_2O$: Dark green triangular crystals were grown by standing a solution of $CoCl_2\cdot 6H_2O$ and **2** in CH_3CN at room temperature. Monoclinic, $P2_1$, a = 11.3742(7), b = 22.355(1), c = 14.5873(9) Å, V = 3589.0(4) Å^3, β = 104.626(1)°, Z = 4, $D_{calc.}$ 1.377 g cm^{-3}. 27064 reflections were collected using a Bruker APEX system at 100 K with Mo–K_α radiation. 12913 unique reflections (R_{int} = 0.019). Data corrected for Lorentzian, polarisation, and absorption (μ = 0.963 mm^{-1}, T_{min} = 0.8598, T_{max} = 1.0). Structure solved by direct methods, and refined against $|F|^2$ using anisotropic thermal displacement parameters for all non-hydrogen atoms (isotropic for the disordered ether oxygen atoms mentioned below). Hydrogen atoms were placed in calculated positions except for those of the water molecule which were not included in the refinement. One of the ether oxygens displayed a large thermal displacement parameter which was modeled as a disorder over two sites with a 0.7/0.3 occupation ratio. Final R factor for 12082 reflections ($I > 2\sigma(I)$) with 822 variables was 0.033 (R_w = 0.079), and the absolute structure parameter 0.006(7). Residual electron density peaks: min. −0.45, max. 0.69 e Å^{-3}. Calculation used the SHELXL76 program. CCDC 203277. See http://www.rsc.org/suppdata/cc/b3/b301267k/ for crystallographic data in .cif or other electronic format.

§ The lowest energy π–π* transition of **2** was calculated to occur around 280 nm and to have its electric dipole transition moment orientated approximately along the C_{imine}–$C_{2\text{-}pyridyl}$ bond, analogous to the long axis polarised transition of 2,2′-bipyridyl.

¶ For example, the distances between the $C_{2\text{-}pyridyl}$ atoms for the two *inter* nuclear chromphore couplings are 6.00 Å and 7.52 Å, compared with 5.42 Å for the corresponding *intra* nuclear distance.

1 U. Knof and A. Von Zelewsky, *Angew. Chem., Int. Ed*, 1999, **38**, 303.
2 B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed*, 2001, **40**, 2022; S. R. Seidel and P. J. Stang, *Acc. Chem. Res.*, 2002, **35**, 972; D. L. Caulder and K. N. Raymond, *Dalton Trans.*, 1999, 1185.
3 The geometry of the $[Co_2Cl_2]$ core is very similar to a previously reported complex: C. Hemmert, M. Renz, H. Gornitzka, S. Soulet and B. Meunier, *Chem. Eur. J.*, 1999, **5**, 1766.
4 A. Rodger and B. Nordén, *Circular Dichroism and Linear Dichroism*, 1997, Oxford University Press, Oxford. See also: B. Nordén, *Inorg. Nucl. Chem. Letters*, 1977, **13**, 355; L. Johansson and B. Nordén, *Inorg. Chim. Acta*, 1978, **29**, 189.
5 M. Ziegler and A. von Zelewsky, *Coord. Chem. Rev*, 1998, **177**, 257; B. Bosnich, *Acc. Chem. Res.*, 1969, 266.
6 A number of other multinuclear complexes have been reported in the literature which have unusual CD spectra (e.g. highly complex spectra and/or of anomolously low intensity compared with mononuclear analogues). For example, see: K. Isele, V. Broughton, C. J. Matthews, A. F. Williams, G. Bernardinelli, P. Franz and S. Decurtins, *Dalton Trans.*, 2002, 3899; X. Hua and A. von Zelewsky, *Inorg. Chem.*, 1995, **34**, 5791; T. J. Rutherford, M. G. Quagliotto and F. R. Keene, *Inorg. Chem.*, 1995, **34**, 3857.We are currently investigating whether an 'internuclear' exciton coupling effect may also be operative in these complexes. Results will be published in due course.